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Effects of the neonicotinoids acetamiprid and thiacloprid in their commercial formulations on soil fauna

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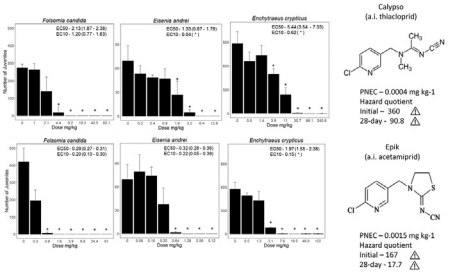
HIGHLIGHTS

- Risk assessment of thiacloprid and acetamiprid using soil invertebrate test battery.
- Initial exposure-toxicity ratios (ETR) are below the trigger values.
- Hazard quotients (HQ) are greater than the trigger value for the European Commission.
- Both ETR and HQ indicate a potential environmental risk for the soil compartment.
- Further research is required to refine risk assessment estimates.

GRAPHICAL ABSTRACT



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ABSTRACT

Neonicotinoids are the most prominent group of insecticides in the world and are commercialized in over 120 countries for the control of agricultural pests mainly due to their broad-spectrum activity and versatility in application. Though non-target soil organisms are likely to be exposed during application, there is paucity of information in scientific literature regarding their sensitivity to neonicotinoids. This study attempts to fill this gap by evaluating, under laboratory conditions, the chronic toxicity of the neonicotinoids thiacloprid and acetamiprid, through their commercial formulations (CF), to the soil invertebrates *Folsomia candida*, *Eisenia andrei* and *Enchytraeus crypticus*. Results obtained indicate that the relative reproductive sensitivity of the test organisms can be expressed as: *F. candida* = *E. andrei* > *E. crypticus* (for acetamiprid CF) and *E. andrei* > *F. candida* > *E. crypticus* (for thiacloprid CF). To extrapolate from laboratory test results to field conditions, predicted environmental concentrations (PECs) and predicted no-effect concentrations were derived. Calculated toxicity-exposure ratios (TER = EC10/PEC) were below trigger values for acetamiprid and thiacloprid, when estimated with initial PEC. While estimated hazard quotients (HQ = PEC/PNEC), were greater than the European Commission trigger value. Therefore, with the current data under standard environmental risk assessment schemes it can be considered that the risk of thiacloprid and acetamiprid to the soil compartment is unacceptable. However, further research into the effects of these substances on different organisms is

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required to increase the confidence in the risk assessment estimates for instance, by calculating hazardous concentrations using species sensitivity distribution curves.

1. Introduction

Neonicotinoids are one of the most effective class of insecticides in the world since the commercialization of pyrethroids, registered in at least 120 countries globally with annual sales estimated at $1.5 billion. As systemic pesticides, they are selective agonists of insect nicotinic acetylcholine receptors (*n*AChRs) (Jeschke et al., 2011; Szczepaniec et al., 2013). Since the early 2000s neonicotinoid use has seen a large increase mostly driven by their use in seed treated with neonicotinoid dressings (Wood and Goulson, 2017). Although 60% of neonicotinoids are used as prophylactic seed dressings, they are also applied as foliar sprays, granular treatments and through chemigation for the control of lepidopteran, coleopteran and hemipteran pest species (Goulson, 2013; Jeschke and Nauen, 2010). Non-agricultural uses of neonicotinoids include professional usage for controlling cockroaches, ants and termites in households, and in veterinary medicine for the topical control of ectoparasites in pets (Jeschke et al., 2011; Goulson, 2013). In comparison to organophosphate and carbamate insecticides, the broad-spectrum insecticidal properties, low mammalian toxicity, high flexibility of use and lower application rates (g of active ingredient per hectare) have led to the widespread use of neonicotinoids (Zalom et al., 2005; Elbert et al., 2008).

Thiacloprid and acetamiprid are two neonicotinoid compounds widely used in agriculture. Thiacloprid is the second member of Bayer's chloronicotinyl insecticide family launched in 2000 under the formulation Calypso®. Acetamiprid was initially commercialized in Japan in 1995 by Nippon Soda. Today, acetamiprid is marketed under several brands such as Mosipilan®, Epik®, Assail® and Chipco™ with different formulations. Both insecticides belong to the same chemical class called cyanoamidines and are mainly utilized for foliar applications, while direct soil use is restricted (Yu et al., 2007; Elbert et al., 2008). In addition, acetamiprid has been more effective against pests (e.g. *Bemisia tabaci*), when used as foliar sprays, than when applied directly to soil (Palumbo et al., 2001). Apart from its selective toxicity to insect pests, thiacloprid is reported to be ecologically benign and its bee safety profile has encouraged its use on flowering plants (Buchholz and Nauen, 2002).

Despite this initial encouragement for thiacloprid use, recent studies have demonstrated that it may not be as safe for bees as initially expected. Thiacloprid has been found to affect, at field realistic doses, honeybees (*Apis mellifera*) immune system (Brandt et al., 2016), their behavior and social interactions (Forfert and Moritz, 2017; Tison et al., 2016, 2017) and colony development (Ellis et al., 2017). For acetamiprid research is scarcer but it was demonstrated to negatively impact the behavior of the honeybee at sublethal doses (Hassani et al., 2008) and has also been found to promote negative molecular effects at environmentally relevant concentrations (Christen et al., 2016). Additionally, whilst not effectively linked to toxic effects, Pohorecka et al. (2017) found, in a study conducted in Poland, that acetamiprid and thiacloprid were the most prevalent insecticides found in colonies winter food stores.

Despite the scarcity of scientific information concerning the toxicity of acetamiprid to aquatic nontarget invertebrates, a review for the European Commission has derived some ecotoxicological values, for *Daphnia magna* (LC50 = 49.8 mg L^{-1} and $NOEC_{chronic}$ = 5 mg L^{-1}) and *Chironomus riparius* ($NOEC_{chronic}$ = 0.005 mg L^{-1}) (EC, 2004b). On the other hand, independent research demonstrated the high toxicity of thiacloprid in aquatic ecosystems. For instance, thiacloprid affected the sediment-dwelling nontarget insect *Chironomus riparius* at concentrations ≥0.5 μg L^{-1} (Langer-Jaesrich et al., 2010). In a different study, the 5% hazardous concentration (HC5) of thiacloprid (0.72 μg L^{-1}) for freshwater arthropods based on acute exposure and chronic post-exposure observations was found to be lower than predicted environmental concentrations ($PEC_{orchard}$: 1.99 μg L^{-1}; $PEC_{ornamental}$: 17.52 μg L^{-1}) for surface water under a worst-case scenario (Beketov and Liess, 2008). The extent of their presence is such that both compounds have been included in a review on neonicotinoid contamination of surface waters (Morrissey et al., 2015). These research findings highlight the need to reduce the potential toxicity of thiacloprid to nontarget freshwater organisms, and that further research is required for these compounds, especially acetamiprid.

In the soil compartment field dissipation studies have revealed that acetamiprid and thiacloprid are easily biodegraded with DT_{50} of 2.9 and 9–27 days respectively in the top soil layer (EC, 2004a, 2008; Barden, 2001). However, a recent review regarding the environmental risk of neonicotinoids has reported that the DT50 values for both compounds is highly variable. For acetamiprid DT50 values ranged from 31 days in the field to 450 in laboratory conditions and thiacloprid from 4 to 27 days in the field to over 1000 days in laboratory conditions, but compared to other systemic pesticides these neonicotinoids are still considered to degrade rapidly in soil (Bonmatin et al., 2015; Goulson, 2013; Wood and Goulson, 2017). This variability can be attributed to different environmental conditions, where soil moisture (lower degradation in dry soil) and pH (higher degradation in acidic soils) where found to affect degradation times (Bonmatin et al., 2015). Furthermore degradation of these compounds is strongly affected by soil microbial activity which is itself variable and can be affected by environmental conditions (Liu et al., 2011). The transformation of acetamiprid and thiacloprid produce metabolites in the soil which have been considered persistent by governing institutions DT_{90} > 100 (EPPO, 2003b; EC, 2004a). In a review by Simon-Delso et al. (2015) the main metabolite for acetamiprid is IMI-4 and known minor metabolites are ACE-urea and 6-CNA. While for thiacloprid the major metabolite is THI-NCONH2 which can be further degraded into THI-NH and THI-SO3-H-NCONH2. Unfortunately, little information is known of their effects towards soil invertebrates and none of these compounds have been highlighted as active towards invertebrates (Simon-Delso et al., 2015). Regarding the toxicity of these compounds to soil invertebrates, a comparable situation is observed to that of the aquatic environment where data on the effects of acetamiprid is lacking whilst some effects of thiacloprid have been recently reported on several invertebrates. For instance, the lethal and sub-lethal effects of thiacloprid and imidacloprid (also a neonicotinoid) in their pure forms has been determined for four soil invertebrates (*Eisenia andrei, Enchytraeus crypticus, Folsomia candida, Oppia nitens* and *Porcellio scaber*) where thiacloprid was always less toxic than imidacloprid and the most sensitive species was *E. andrei* with an EC50 of 0.44 mg/kg (de Lima